Hybridation between Heterogeneous Photocatalysis and Adsorption

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Abstract

The concept of a hybrid process resulting of the association from the photocatalytic and the adsorption principles opens various opportunities for the design of efficient detoxification processes. One option particularly attractive in the case of solar applications consists in developing a storage function thanks to the adsorbent and its adsorption capacities. As for any solar process, such a property is essential for the design of efficient photocatalytic water treatment. Before optimization of a hybrid process, preliminary studies necessary were carried out in a close fluid loop connecting a photocatalytic reactor based on supported TiO2 and a separate cell filled with a commercial activated carbon. With the 2-4 dichlorophenol selected as a model pollutant molecule, a series of successive cycles corresponding to dark adsorption followed by photocatalysis under UV irradiation was performed. The initial results are promising and indicate that the activated carbon is regenerated reproducibly thanks to photocatalysis. The coupling phenomenon has been explored numerically with mass balances applied to the liquid and the adsorbed phase.

Keywords

Heterogenous Photocatalysis; Activated Carbon; Hybridation; Simulation.

Introduction

Heterogeneous photocatalysis belongs to the advanced oxidation processes family (AOPs). Photo-excitation of TiO2 under ultraviolet radiation initiates surface radical reactions (De Lasa et al, 2005, Zhang et al, 2012). The extremely reactive radicals produced initiate reactions for the mineralization of organic pollutant molecules. Combined with a direct use of solar radiation for the activation of TiO2, this process is in good agreement with the principle of sustainable development. Solar detoxification (Blanco and Malato, 2003; Bahnemann, 2004; Malato et al, 2009) operates according a batch mode. The polluted solution flows in a closed loop between a photocatalytic reactor and a vessel and the treatment is performed until the pollutant concentration reaches the desired value. Feasibility of the mineralization of many organic pollutants has already been demonstrated in the literature (Blake, 2001). Today, the low capacity treatment of this process (Corriea et al, 2011, Plantard et al, 2012), especially in the case of a direct use of solar radiation, is probably one of the major bottlenecks that prevent its dissemination. Water treatment by adsorption does not suffer from this drawback. It is currently involved in many industrial processes such as waste water treatment and drinking water production (Ali and Gupta, 2007, Diaz et al, 2007, Karanfil, 2006). Polluted solutions flow through tanks or columns containing sorbents as activated carbon and the contaminants are separated from the solution by adsorption in the microporous solid. Nevertheless, with this process, the organic compounds are transferred from the solution to the sorbent. When saturated, the activated carbon is, either regenerated with high temperature, a highly consumption energy process, or considered as a solid waste to be incinerated.

The concept of a hybrid process resulting of the association of an AOP with adsorption opens various opportunities for the design of efficient detoxification process. In the literature, it has been largely investigated not only for ozonation (Pocostales et al, 2012; Hang Kim et al, 1997, Alvarez et al, 2009) but also for Fenton's processes (Toledoet al, 2009; Okawaet al, 2007) as well as catalytic wet air oxidation (Delmas, et al, 2009). In the case of heterogeneous photocatalysis, it was often tested as a mean accelerating and

promoting the kinetics of degradation (Matos et al, 2001 Cordero et al, 2007; Carpio et al, 2005). This effect could be expected thanks to an increase of the volumetric concentration of the pollutant (in adsorbed phase) around the photocatalyst, coupled with an efficient transfer of the adsorbed pollutant from the adsorbent to TiO2. A second way to consider the hybridation is based on the fact that, as any chemical reactions, the kinetics of photocatalytic degradation is highly dependent on the level of the molecule concentrations. To avoid the low kinetics rate at the end of a photocatalytic treatment, the interest of the implementation of a column of activated carbon as a post-photocatalytic treatment has recently been tested (Areerachakul et al, 2007; Atheba, 2009). In the present paper, a new option has been explored. With the global and middle term objective to design continuous photocatalytic process based on the solar energy, it is necessary to manage the intermittency and discontinuity of the UV resource. Basically, and whatever the different time scales considered are i.e. the seasonal cycle; the day/night cycle ; the fluctuations due to the local weather conditions, the activated carbon can provide this necessary storage function. When the solar resource is not high enough to provide an efficient photocatalytic treatment, one part of the pollutant is stored by adsorption in the porous network of the activated carbon. When the solar intensity is widely available, the photocatalytic process provides the depollution of the effluent and the activated carbon regeneration. According to this working mode, solar photocatalysis has to be operated as a regeneration way for the sorbent. Then, before any optimization of the hybrid process, preliminary studies are necessary. To achieve this objective, an experimental set up was used to test if an activated carbon previously saturated with a pollutant may be totally or partially regenerated with the help of a heterogeneous photocatalytic reactor. Besides this experimental part, the coupling phenomenon between desorption and photocatalytic degradation is modeled with the mass balances applied to the pollutant in the liquid and the adsorbed phase. The concentration profile in the adsorbed phase during regeneration, simulated thanks to the resolution of the set of differential equations, provides quantitative and useful information.

Experimental

The pollutant selected for the tests was 2-4 Dichlorophenol (2-4 DCP), a molecule involved in the pesticides formulation. The photocatalytic media manufactured by Ahlstrom consisted in TiO2 supported on a cellulosic matrix (Paper Grade 1048). The activated carbon, the adsorbent, was a powder (Pica Hydro S-23) with a specific surface area about 1250 $m^2.g^{-1}$. The raw material was crushed and sieved between 80 and 100   m. Before use, the activated carbon powder was out gassed under vacuum at 200°C.

The experimental set up for heterogenous photocatalytic experiment was detailed in a previous paper (Goetz et al, 2009)and consisted of a close fluid loop connecting a cylindrical photocatalytic reactor in borosilicate glass (=9 mm) to a storage tank (1 liter). Aqueous 2-4DCP solution flowed through the reactor inside an annular space defined by the internal surface of the reactor tube and an inner tube (=5 mm) with the photocatalytic media (S = 0.0112 m2) wrapped around. Irradiation was provided along the reactor with an UV lamp at 365 nm delivering a radiation UV flux I equal to 32 $W.m^{-2}$, in the range of a UV solar flux available. Uniform irradiation at the surface of the tube was obtained thanks to a CPC collector placed at the back side of the reactor. For the test of the hybrid process, a separate cell filled with the activated carbon (26 mg) was placed in series in the fluid loop (Fig. 1).
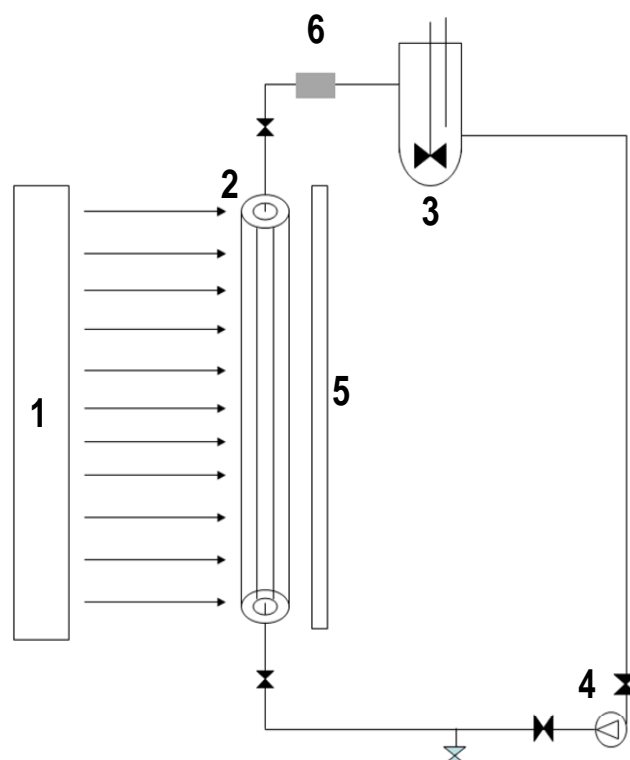

FIG 1: EXPERIMENTAL SET UP: 1 UV LAMP 960 MM IN HEIGHT; 2 ANNULAR REACTOR; 3 STIRRED TANK; 4 VOLUMETRIC PUMP; 5 COMPOUND PARABOLIC COLLECTOR; 6 CELL WITH ACTIVATED CARBON.

Adsorption isotherms of 2-4 DCP in the both materials were obtained from preliminary experiments. The same weights of activated carbon or photocatalytic media were put into stirred Erlenmeyer flask with different initial concentrations of 2-4DCP. Liquid samples were taken and analysis. In the case of activated carbon powder, a couple of hours is necessary to reach equilibrium conditions between the adsorbed and the liquid phases.

In all cases, the concentrations in 2-4DCP were analyzed using reverse-phase liquid chromatography equipped with UV detection (Jasco UV-970M) by means of an Inerstil ODS-3 AIT column. The mobile phase composition and wavelength are acetonitril/ultra-pure water/trifluoroacetic acid at 60/40/0.05 ratio (v/v/v) at 284 nm. The high pressure pump is Merck L-6000 and the automatic syringe is Spark Holland Midas.

Results and Discussion

Adsorption Isotherms

Adsorption isotherms of the two raw materials were determined (Fig. 2). For the photocatalytic media, it was chosen to select the total surface as reference in the expression of the amount of 2-4DCP adsorbed qepm (mole.m^{-2}). As shown in the figure and in the range of concentration studied, adsorption isotherm on the photocatalytic media follows the Henry's law (Eq. 1). As expected, the activated carbon provides a much higher adsorption capacity owing to its microporous texture. 2-4 DCP adsorption in Pica-Hydro S23 follows the classical type I and is well represented by the Langmuir model (Eq. 2).

$$qe_{pm} = H_{ads} \cdot C \qquad\qquad (Eq.\ 1)$$

$$qe_{AC} = \frac{b \cdot Q_m \cdot C}{1 + b \cdot C} \qquad\qquad (Eq.\ 2)$$

With H_{ads} = 0.015 (m) the Henry constant of 2-4 DCP adsorption (mole.m^{-2}) with the photocatalytic media surface is taken as reference, b = 400 m^3.kg^{-1} and Q_m=2.3 mole.kg^{-1}.

Photocatalysis Experiments

Before the operation of the experiment devoted to the hybrid process, an experimental degradation of 2-4DCP without the cell containing activated carbon included in the closed loop was performed. For this test (Fig. 3), the UV lamp was turned on after a dark period once adsorption equilibrium between the photocatalytic media and 2-4DCP was reached.
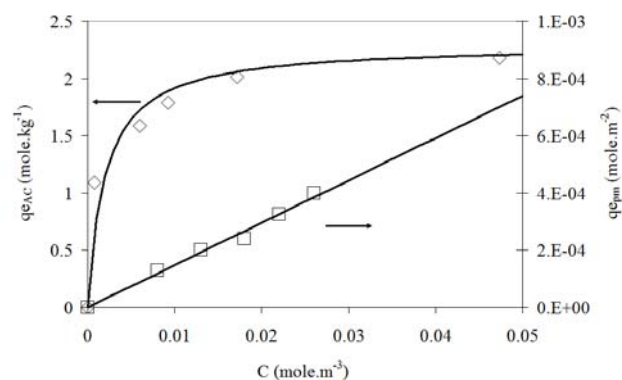

FIG 2: EXPERIMENTAL ADSORPTION ISOTHERMS FOR THE PHOTOCATALYTIC MEDIA (□, RIGHT SCALE) AND THE ACTIVATED CARBON (◊, LEFT SCALE). CONTINUOUS LINES (-) ARE CALCULATED ISOTHERMS WITH EQS. 1 AND 2.

The rate of degradation and the preceding dark adsorption were simulated according to the model previously developed in the case of atrazine degradation (Goetz et al, 2009). The model involves a coupling between the mass transfer of the pollutant from the fluid to the surface of the photocatalytic media, and the photocatalytic degradation. In the formulation, mass transfer is treated by the linear driving force model (Yang, 1987). The kinetic is supposed to be of one order according to the amount of pollutant adsorbed with a kinetic constant directly proportional to the irradiation I :

$$\frac{dC}{dt} = -\frac{V_r}{V_T} \cdot S_{pm} \cdot K_{pm} \cdot (qe_{pm} - q_{pm}) \qquad (Eq.\ 3)$$

$$\frac{dq_{pm}}{dt} = K_{pm} \cdot (qe_{pm} - q_{pm}) - (\alpha \cdot I) \cdot q_{pm} \quad (Eq.\ 4)$$

With V_r and V_T respectively the reactor and total fluid loop (including the storage tank) volumes, S_{pm}, the photocatalytic media surface per unit of reactor volume (m^2.m^{-3}) and K_{pm}, the mass transfer coefficient are defined according to the solid phase.

The two parameters necessary for the simulation were identified separately to find the fit between the experimental and the calculated concentration profiles of 2-4 DCP in the solution. K_{pm} was determined during the dark adsorption phase (K_{pm} = 4 10^{-3} s^{-1}) when the value of the irradiation I is equal to zero. Keeping the value of K_{pm} identified during the dark phase, the kinetic constant   is estimated during the degradation under UV irradiation   = 1.4 10^{-5} m^2.J^{-1}).

Mass transfer involves taking into account the adsorption properties of the photocatalytic media as well as the reactor configuration and the media

implementation (isotherm, mass transfer coefficient that partly depends on the mass flow conditions). Such a formulation is necessary to represent the preliminary phase of adsorption (Fig.3). The coupling between mass transfer and the kinetic of degradation when the reactor is irradiated leads to a set of the two ordinary differential equations (Eqs. 3-4).
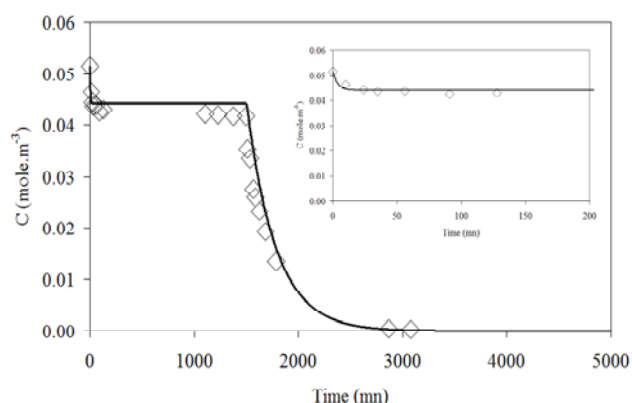

FIG 3: EXPERIMENTAL CONCENTRATION (□) AND SIMULATED ONE (-), EXPERIMENT WITH ONLY THE PHOTOCATALYTIC MEDIA.

If one neglects the accumulation of pollutant adsorbed in the photocatalytic media (less than 10%) and one adopts the pseudo-steady-state hypothesis for the adsorbed phase ($dq_{pm}/dt=0$), the system reduces to:

$$\frac{dC}{dt} = -\frac{V_r}{V_T} \cdot S_{pm} \cdot \frac{qe_{pm}}{(1/K_{pm} + 1/(\alpha \cdot I))} \qquad \text{(Eq. 5)}$$

Considering the adsorption isotherm, it leads to an expression involving the concentration of the pollutant in the bulk phase C and an "apparent kinetics constant" depending on the two values characteristic of the coupling:

$$\frac{dC}{dt} = -\frac{V_r}{V_T} \cdot S_{pm} \cdot \frac{H_{ads} \cdot C}{(1/K_{pm} + 1/(\alpha \cdot I))} \qquad \text{(Eq.6)}$$

For the case studied, and the working conditions adopted (level of irradiation, flow regime), and according to the values previously identified, the mass transfer limitation ($1/K_{pm}$) is almost negligible in comparison with the kinetic limitation ($1/(\alpha.I)$). The rate of degradation could be approximated with the classical pseudo first order law according to the pollutant concentration and an "apparent constant" proportional to the irradiation.

Cycles of Saturation and Photocatalytic Regenaration

Following this preliminary experiment, a series of successive cycles was performed to study the activated carbon regeneration thanks to photocatalysis (Fig. 4). With the cell containing the adsorbent included in the fluid loop, at the beginning of each cycle, the storage tank was filled with one litre of solution with an initial concentration of 2-4 DCP equal to 0.09 mol.m-3 (15 mg.l-1). For each cycle, a phase of adsorption in the dark was running during almost 24 hours. Such long duration to reach the equilibrium condition is necessary because of the small residence time of the solution in the cell containing the adsorbant in comparison with the experimental time. Then, photocatalysis was started turning on the UV lamp.

At the beginning of the first cycle, the activated carbon was free of any pollutant. It was previously out gassed under vacuum at 200°C. There was a maximum amount of pollutant adsorbed during the dark phase. At the end of the adsorption phase, the concentration in the liquid phase is around 0.02 mole.m^{-3}. The equilibrium condition was in agreement with the adsorption isotherm determined previously. After 1500 mn, (90 10^3 s), the UV lamp was turn on, degradation happened and the concentration of 2-4 DCP in the liquid phase decreased (Fig. 3). 2,4 DCP concentration in the liquid phase was close to zero after 500 mn. Nevertheless, one has to keep in mind that the real time of irradiation has to take into account the ratio of the reactor volume by the total fluid loop volume. The irradiation was continued because even if 2-4 DCP was not detected in the solution, it was still adsorbed on activated carbon. In this condition desorption should occur because of the out of equilibrium condition. The driving force for the desorption was the difference C between the concentration of 2-4 DCP in the liquid bulk phase and the concentration in equilibrium with the adsorbed phase. It was maintained by mean of the degradation of 2-4 DCP in the solution by photocatalysis. Nevertheless, the steep shape of the adsorption isotherm at low amount of 2-4 DCP adsorbed (Fig. 2) necessarily limits the absolute value of C and, as a result, the rate of desorption. This is the reason why the photocatalytic degradation was continued a long time after the concentration in the liquid phase reach a value very close to zero. The total duration of experimentation is equal to 6000 mn.

After the first cycle, additional cycles were carried out. All the liquid was removed and replaced by a fresh solution of 2-4 DCP ($C_{initial}$=0.09 mole.m^{-3}). After having change the solution and before turning on the UV irradiation, the solution was circulated in the loop, then the concentration of 2-4 DCP was stabilised close

to 0.04 mole.m^{-3} versus 0.02 mole.m^{-3} for the first cycle. During dark adsorption, the difference in the profiles of concentration between the first and the following cycles was the result of the 2-4 DCP still adsorbed at the end of regeneration. Since the concentration was higher after successive cycle, then less 2-4 DCP was adsorbed on activated carbon. Indeed, the amount adsorbed for the first cycle was about q = 2 mole.kg^{-1} whereas, the amount adsorbed for the following cycle was about q = 1.3 mole/kg^{-1}. Hence in the experimental conditions tested, a regeneration rate of 65% was reached. In addition, the reproducibility of the kinetic suggested that there was no by-products that compete with adsorption sites of 2-4 DCP. The desorption phenomenon was reproducible.
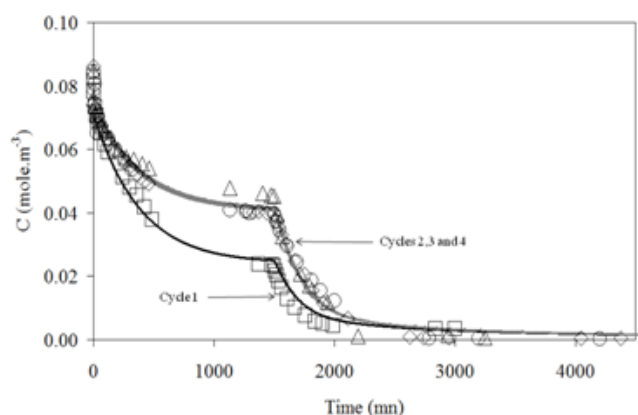

FIG 4: EXPERIMENTAL (PHOTOCATALYYIC MEDIA + ACTIVATED CARBON) CONCENTRATION PROFILES DURING THE CYCLES 1 (□); 2(○); 3(◇); 4(△) AND CORRESPONDING SIMULATIONS (-).

Coupling sorption of a pollutant with activated carbon and photocatalysis has often been explored in the literature with the objective to obtain a synergetic effect, i.e., an increase of the degradation kinetic (Matos, 2001, Tryba, 2003, Liu, 2007, Leee, 2004). As a consequence, quite a few papers have been focused on the regeneration. Recently and in the particular case of the solar regeneration of composites (powdered activated carbon impregnated with photocatalyst) reproducible regeneration efficiency between 40 and 80% is reached (Yap, 2012) depending on the pollutant studied.

Basically, regeneration can happen only for a physical and reversible sorption of the pollutant in the micropores of the activated carbon. In that case, adsorption as well as desorption of 2-4 DCP, should be well represented by the linear driving force model applied with the mean amount of pollutant adsorbed in the microporous texture (Yang, 1987). Considering this formalism, the mass balances applied to 2-4 DCP

in the liquid and the adsorbed phase lead to:

$$\frac{dC}{dt} = -\frac{V_r}{V_T} \cdot S_{pm} \cdot K_{pm} \cdot (qe_{pm} - q_{pm}) - \\ \frac{V_{Ac}}{V_T} \cdot \rho_{AC} \cdot K_{AC} \cdot (qe_{AC} - q_{AC}) \qquad \text{(Eq. 7)}$$

$$\frac{dq_{AC}}{dt} = K_{AC} \cdot (qe_{AC} - q_{AC}) \qquad \text{(Eq. 8)}$$

These two mass balances associated to equation 4 (unchanged) define the set of differential equations representative of the working of the process coupling sorption and photocatalysis. The only one unknown parameter is the mass transfer parameter K^{AC}. As previously, it was identified (K$_{AC}$=4 10^{-5} s^{-1}) to find the best fit between the simulated and the experimental concentration profiles of 2-4 DCP in the liquid phase during the different cycles. For the first cylcle, the initial amount of 2-4 DCP adsorbed was equal to zero. For the following cycles, the initial values (q$_{pm}$, q$_{CA}$) were taken equal to the values calculated at the end of the regeneration phase of the previous cycle. As shown in figure 4, the model allows a reasonable good agreement of the simulated values with the experimental ones. In fact, it is necessary to keep in mind that this model is based on important simplifying assumptions such as no competition at all between the pollutant molecule and the by-products of degradation.

The adsorbed quantities of the pollutant molecules simulated as a function of the time and the cycle number are presented on figure 5. At the end of the first degradation phase occurring between 1500 and 6000 mn, pollutant molecules are still adsorbed. This is the physical explanation of the difference between the first and the following cycles. Regeneration becomes more and more difficult when the quantities adsorbed diminished. Desorption rate decreases in relation with the decrease of the equilibrium gap. Indeed, basically, desorption happens because of the difference between the concentration of 2-4 DCP in the bulk phase and its concentration at the surface of the activated carbon pellet, i.e., the equilibrium gap. It is represented by equation 8 according to the linear driving force formulation. For low value of concentration in the bulk liquid phase and low amount of 2-4 DCP adsorbed, the shape of the isotherm necessarily entails a very low equilibrium gap and as a consequence a very low flux of desorption. The comparisons of the concentration and the adsorbed profiles as a function of the time bring to light the important gap that exists

between these two values. Liquid concentration of 2-4 DCP cannot be considered as representative of the rate of regeneration. At 2000 mn (Fig. 4), 2-4 DCP had almost disappeared the solution. At this time the activated carbon was far being regenerated (Fig. 5). For the case studied (reactor configuration, mass of activated carbon, level of irradiation…), the mass transfer of 2-4 DCP from the adsorbed phase in the micropores to the liquid phase was clearly the phenomenon limiting regeneration. This result does not contradict the principle of development of a hybrid process. As for any coupling between two or several mechanisms, to match the desired objective, the process will have to be designed taking into account the most limiting phenomenon.
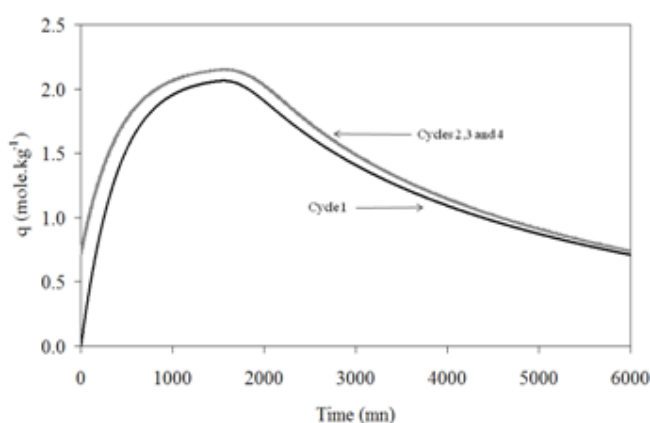

FIG 5: SIMULATED ADSORBED AMOUNT OF POLLUTANT IN ACTIVATED CARBON DURING CYCLE AND CYCLES 2, 3. FOR ALL CYCLES UV IRRADIATIONS WAS TURNED ON AT t=1500 mn.

Conclusion

The concept of hybridation between sorption and advanced oxidation processes is attractive for water treatment processes, which makes it possible to design a storage function perfectly integrated. Then, and whatever the final targeted application, industrial or urban wastewater is, it would be very useful for these processes basically subjected to important variations in the mass flows to be treated. Such a storage function is particularly critical in the case of detoxification with solar heterogeneous photocatalysis. Indeed, this process provides the unique opportunity to improve the sanitary level of polluted effluents at almost zero energy cost, but it is based on the use of a limited and highly discontinuous resource.

Based on the experimental results obtained, the principle of regeneration of an activated carbon previously charged with a pollutant molecule seems to

be realistic with regard to the reproducible cycles of saturation/regeneration of the adsorbent. The model developed based on the coupling between mass transfer and photocatalytic degradation leads to a physical interpretation of the different mechanisms involved in the coupling phenomena. Despite the numerous assumption and simplification, it is representative of the concentration profiles during regeneration. Such a model can be a useful tool in the selection of an activated carbon particularly adapted to the saturation and the regeneration by a given pollutant and/or mixture of pollutants. Obviously, the experimental and theoretical results presented in this paper have to be considered as preliminary but promising results,and have to be confirmed with many complementary experiments to perform with different initial levels of concentration, different pollutant molecules, performance indicators (TOC, COD, …), and finally, activated carbon developing different microtextures. This last point is particularly relevant. Microtexture should greatly influence the shape of the pollutant adsorption isotherm and as the consequence, the ability of the activated carbon to be regenerated efficiently thanks to solar heterogeneous photocatalysis.

NOTATIONS

C : concentration of pollutant ($mol.m^{-3}$)

I : UV irradiation of the reactor ($W.m^{-2}$)

K : mass transfer coefficient (s^{-1})

q : pollutant adsorbed ($mol.m^{-2}$; $mol.kg^{-1}$)

qe : pollutant adsorbed in equilibrium with the bulk phase ($mol.m^{-2}$; $mol.kg^{-1}$)

S : surface of photocatalytic media   (m^2).

S_{pm} : surface of photocatalytic media per unit volume of reactor ($m^2.m^{-3}$)

VAC : activated carbon volume (m^3)

V_r : reactor volume (m^3)

V_T : total volume of the fluid loop (m^3)

        : kinetic constant ($m^2.J^{-1}$)

        : activated carbon density ($kg.m^{-3}$)

Subscript

pm : photocatalytic media

AC : activated carbon

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